

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



Serial No. 10/640,853
Confirmation No. 9178
Group No. 3763

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C08L 75/08, A41D 19/00	A1	(11) International Publication Number: WO 89/ 03860 (43) International Publication Date: 5 May 1989 (05.05.89)
(21) International Application Number: PCT/US88/03577 (22) International Filing Date: 12 October 1988 (12.10.88) (31) Priority Application Number: 108,423 (32) Priority Date: 14 October 1987 (14.10.87) (33) Priority Country: US (71) Applicant: TYNDALE PLAINS-HUNTER, LTD. [US/US]; 29 Cedar Lane, Princeton, NJ 08540 (US). (72) Inventors: FAUST, Ellsworth, E. ; 914 Edgewood Road, Yardley, PA 19067 (US). KLIMENT, Charles, K. ; 321 Walnut Lane, Princeton, NJ 08540 (US). GOULD, Francis, E. ; 29 Cedar Lane, Princeton, NJ 08540 (US).		(74) Agent: SCHMONSEES, William; Ratner & Prestia, Suite 412, Leighton Building, 500 North Gulph Road, P.O. Box 980, Valley Forge, PA 19482 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MOISTURE SENSITIVE ELASTOMER COMPOSITIONS (57) Abstract <p>Elastomer compositions, having water absorptive properties, are produced by subjecting a homogeneous blend of a curable rubber latex and a hydrophilic polyurethane polymer, to curing conditions. Moisture permeable membranes, water swellable sealants, extruded shapes and active agent media are produced from the composition.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

5

10

15

MOISTURE SENSITIVE ELASTOMER COMPOSITIONS

Technical Field

20

This invention relates to elastomer compositions. More particularly, the invention pertains to moisture sensitive elastomer compositions comprising a composite of a rubber polymer and a hydrophilic polyurethane polymer.

25

Background of the Invention

It is well known that rubber, including natural and synthetic types, as a class is highly resistant to the effects of moisture. In fact, rubber is the material of choice for fabricating a great

-2-

5 variety of water repellant articles, particularly
fabrics and coatings. However, there are some
applications for which a moisture sensitive rubber is
desirable. For instance, rubber films and membranes
10 having increased moisture permeability and
transmission would be useful in fabricating
prophylactic devices such as condoms as well as
bandages, finger cots and surgical gloves. Rubber
that absorbs water accompanied by swelling would be
15 useful as self-sealing caulks and gaskets in an
aqueous environment. Because of their relatively high
water absorbency, these materials would also be
suitable for holding and controlling the release of
active ingredients as exemplified by medications,
flavors, fragrances, insecticides, germicides,
spermicides and the like.

Disclosure of the Invention

20 It has now been discovered that moisture
sensitive rubber compositions can be realized by
combining rubber with a hydrophilic polyurethane
polymer. The provision of such compositions and their
25 preparation and uses constitute the principal objects
and purposes of the invention. Other objects and
purposes will become apparent in the ensuing
description.

-3-

As employed herein, the expression "moisture sensitive" means that the rubber compositions of the invention undergo changes in physical behavior such as swelling on exposure to a moist environment such as body fluids or tissues. Examples of these changes and how they can give rise to useful properties are described above and hereinafter.

The moisture sensitive rubber compositions of the invention are prepared by first forming a homogeneous blend of a curable rubber component and a hydrophilic polyurethane and then subjecting the blend to curing conditions to effect curing of the rubber component. In some formulations, the curing conditions may cause crosslinking of the polyurethane component as well.

In preparing the blends, efforts should be made to ensure that the two basic components are thoroughly mixed. A generally suitable procedure consists in mixing the curable rubber component (in the form of a rubber latex or as a solution or dispersion in an organic solvent) with a solution or water-based emulsion of the hydrophilic polyurethane polymer. Curing of the composition is performed in the usual manner, i.e., by heating in the presence of rubber curing agents. Exemplary and satisfactory curing agents include sulfur, zinc oxide, dimethyl zinc and methyl or ethyl dithiocarbamate or any mixture thereof. In a typical curing operation, the

-4-

uncured blends including the curing system are first stripped of volatile components such as water or solvents. The stripped blends can then be pressure formed or extruded to give the desired shape. In the case of films or membranes such as condoms or gloves, dipping or casting is the usual forming method. The foregoing and other rubber shaping techniques are well known in the art and therefore need not be described in detail. Once the final configuration is obtained, curing is effected by applying heat.

As understood herein, the term "curable rubber component" includes uncured natural rubber as well as various synthetic curable rubber components commonly used in the preparation of synthetic rubbers and elastomers. Representative synthetic rubber components include those derived from unsaturated hydrocarbon monomers and mixtures thereof, such as isoprene, chloroprene, butadiene, SBR (styrene/butadiene rubber), isobutene/isoprene and EPDM (ethylene/propylene/butadiene). Synthetic rubber monomers and latices produced therefrom, as well as other chemicals used in the manufacture of rubber and useful in the invention, are well known and are commercially available from a number of chemical suppliers. A lengthy description of these materials is, therefore, unnecessary for the practice and understanding of the invention. For a comprehensive review of rubber and rubber technology, describing

-5-

rubber components and methods useful herein, see Kirk-
Othmer, Encyclopedia of Chemical Technology, Third
Edition, Vol. 20, particularly pages 337 to 489
(incorporated herein by reference).

The hydrophilic polyurethane polymers
employed in carrying out the invention are known
materials, the description and preparation of which
are set forth, for example, in U. S. Patent Nos.
3,822,238, 3,975,350, 4,156,066, 4,156,067, 4,255,550,
4,359,558 and 4,451,635, incorporated herein by
reference. Such polymers are resins obtained by
reacting a polyisocyanate with a resin having two or
more reactive terminal hydrogens and containing
various polar sites which appear in the final polymer
product and are responsible for its hydrophilic
character. Illustrative polar sites include ether
groups, carboxylic acid groups, sulfhydryl groups,
sulfonium groups, sulfonic groups and quaternary
ammonium groups.

Representative resin systems from which the
hydrophilic polyurethane polymers can be derived are:

1. An adduct of dihydroxy compounds such as
ethylene glycol or propylene glycol with ethylene
oxide, propylene oxide, ethylene imine, propylene
imine, dioxolane or any mixtures of same;

-6-

2. An adduct of trihydroxy compounds such as glycerol or trimethylol propane with ethylene oxide, propylene oxide, ethylene imine, propylene imine, dioxolane or any mixtures of same;

3. An adduct of tetrahydroxy compounds such as erythritol or pentaerythritol with ethylene oxide, propylene oxide, ethylene imine, propylene imine, dioxolane or any mixtures of same;

4. An adduct of polyhydroxy compounds such as anhydroenneaheptitol, sorbitol, mannitol, hydrolyzed low molecular weight polyvinyl acetate, sucrose or lactose with ethylene oxide, propylene oxide, ethylene imine, propylene imine, dioxolane or any mixtures of same;

5. An adduct of polybasic acids such as trimellitic acid, pyromellitic acid, mellitic acid, pyrophosphoric acid, and low molecular weight polyacrylic and methacrylic acids with ethylene oxide, propylene oxide, ethylene imine, dioxolane or any mixtures of same;

6. An adduct of hydroxy acids such as maleic acid, citric acid or sugar acids with ethylene oxide, propylene oxide ethylene imine, dioxolane or mixtures of same. Sugar acids are defined in "Carbohydrate Chemistry," Volume 5 and more

-7-

specifically, Chapter 17 (a review of literature published during 1971), The Chemical Society, Burlington House, London, Great Britain (1972) and in other sources as well;

7. An adduct of amino compounds, such as ammonia, ethylene diamine, diethylene triamine, triethylene tetraamine with ethylene oxide, propylene oxide, ethylene imine, dioxolane or any mixtures of same;

8. Hydrammonium or quaternary ammonium salts of 7;

9. A sulfonated polyester resin of maleic acid, itaconic acid, mesaconic acid, fumaric acid and a glycol of 2 to 6 carbon atoms;

10. A polyester of a lower alkyl dialkanolamine and a diacid wherein the diacid is adipic, sebacic, azelaic, maleic, phthalic, fumaric acid or mixtures of same, the amine group being converted to an hydraammonium or quaternary ammonium group;

11. A linear or slightly branched polyamide of an alkyl amine and a diacid wherein the amine is diethylene triamine, triethylene tetraamine, tetraethylene pentamine or polyloweralkylene imines

-8-

such as ethylene imine or propylene. Suitable diacids include maleic, adipic, azelaic, sebacic, phthalic, itaconic acid or any mixture of same. The term "slightly branched" indicates only methyl or ethyl substituents on the polyamide backbone, the ethyl substituent being less than 1%;

12. Hydrammonium or quaternary ammonium salts of 11;

13. Polysulfhydryl resin having in the backbone sulfonium, sulfoxide, or sulfone groups;

14. Hydrammonium or quaternary ammonium salts of ethylene or propylene imine adducts of polyhydroxy compounds from categories 1 to 4; and

15. Polyesters of poethylene oxides with maleic acid, adipic acid, sebacic acid, phthalic acid, azelaic acid, fumaric acid or any mixtures of same.

In general, the resins of classes 1-15 above will fall within an equivalent weight range above 140, preferably above 170 and up to about 2000. In addition, a ratio of carbon atoms to oxygen and/or amine and/or imine nitrogen atoms ranging from about 1.2:1 to about 2.8:1 is required. Preferably, the ratio is 1.33:1 to 2.8:1, more preferably 1.33:1 to 2.5:1.

-9-

5 The aforescribed polyurethane polymers may
vary in their hydrophilicity from polymers that are
water soluble to polymers which are water insoluble
but which nevertheless will absorb water (e.g., at
least 10% by weight) usually accompanied by swelling.
Hydrophilic character can be controlled by balancing
the type and number of polar sites against the type
and size of the inert portion of the polymer molecule
10 following the guide lines given in the cited patents.

15 A representative polyurethane useful in the
invention is prepared by reacting a diisocyanate with
a mixture of one or more low molecular weight alkylene
glycols such as diethylene glycol and one or more
long-chain polyoxyalkylene glycol resins in which the
oxyalkylene units contain 2 to 4 carbon atoms.
Hydrophilic character in these polyurethanes is
determined by varying the ratio of low molecular
20 weight alkylene glycol and long-chain polyoxyalkylene
glycol. Extreme hydrophilicity of the polymer, even
water solubility, is achieved by employing a
predominant amount of the highly polar polyoxyethylene
glycol. Minimal hydrophilicity results when employing
25 a predominant amount of a polyoxyalkylene glycol in
which the oxyalkylene contains higher numbers of
carbon atoms, that is, three or more. Intermediate
hydrophilicity can be realized by using a mixture of
the polyoxyalkylene glycols or glycols having varying

-10-

ratios of high to low oxyalkylene units in the resin chain.

5 A highly suitable hydrophilic polyurethane
polymer for preparing the moisture sensitive rubber
compositions of the invention comprises the reaction
product of a mixture of an organic diisocyanate, a low
10 molecular weight alkylene glycol, such as ethylene
glycol and/or diethylene glycol, a water-soluble
poloxyethylene glycol having a number average
molecular weight of from about 400 to about 20,000,
and water, the reaction mixture having an NCO/OH ratio
of from about 0.5 to 1.0, preferably about 0.8 to 0.98
15 and wherein the percent by weight in the reaction
mixture of the low molecular weight glycol is no more
than about 20%, the water content is no more than
about 0.5% and the weight percent of the diisocyanate
is from about 5% to about 60%.

20 An especially preferred polymer is produced
by reacting on a 100% weight basis from about 12% to
about 55% of methylene bis(cyclohexyl-4,4'-
isocyanate), from about 2% to about 20% of the low
25 molecular weight alkylene glycol such as diethylene
glycol, from about 25% to about 85% of a
polyoxyethylene having a number average molecular
weight of from about 1000 to about 8000 and from about
0.1% to about 0.5% water.

-11-

In addition to methylene bis(cyclohexyl-4,4'-isocyanate) other diisocyanates can be used in preparing suitable hydrophilic polyurethane polymers. These other diisocyanates include both aliphatic and aromatic types although the aliphatics are preferred. Representative members are tetramethylene diisocyanate, hexamethylene diisocyanate, trimethylhexamethylene diisocyanate, cyclohexylene 1,2-diisocyanate, cyclohexylene 1,4-diisocyanate, and aromatic diisocyanates such as 2,4- and 2,6-tolylene diisocyanates. Also suitable are the isocyanate equivalents which form urethane linkages as exemplified by nitrile carbonates, such as adiponitrile carbonate.

The alkylene glycols and polyoxyalkylene glycols are known entities which can be purchased from chemical supply houses. Typical commercial products are the polyoxyethylene glycols manufactured by the Union Carbide Corporation, such as CARBOWAX® 1450, CARBOWAX® 4500 and CARBOXWAX® 8000. The numbers refer to average molecular weights.

In preparing the hydrophilic polyurethane polymers, the glycol components and water are formed into a homogeneous mixture which is then reacted with the diisocyanate. The reaction is catalyzed by known catalysts, examples of which are tin salts and organic tin esters such as dibutyl tin dilaurate, tertiary

-12-

amines such as triethyl diamine (DABCO), N,N,N,N'-tetramethyl-1,3-butane diamine, and other recognized catalysts for urethane polymer synthesis.

5 The presence of water in the reaction mixture causes evolution of carbon dioxide, resulting in the polymer being obtained as a foam. This is an advantage in that the foamed polymer, owing to its large surface area, exhibits a high rate of
10 dissolution, thereby facilitating the preparation of solutions of the polymer.

15 In adding the requisite quantity of water to the reaction mixture, allowance should be made for any moisture that may be present in the glycol components. It is not unusual for commercial grades of alkylene glycols and polyoxyalkylene glycols to contain varying amounts of water. Moreover, such glycols tend to be
20 hygroscopic and even if free of water, may become contaminated with moisture from atmospheric exposure. Preferably, however, sufficient water will be present or added to cause foaming of the polyurethane polymer as it is formed. Generally, from about 0.1 to about 0.5 part by weight of water based on 100 parts by
25 weight of the total reaction mixture will be effective.

 So far as can be ascertained, the compositions of the invention should generally contain

-13-

at least about 50% by weight of the hydrophobic rubber component in order to provide the requisite elasticity or rubbery character. Such formulations are preferred when the compositions of the invention are used in the manufacture of prophylatic devices and other film articles requiring a high rate of water vapor transmission.

Depending on their chemical configuration, the hydrophilic polyurethane polymers may be insoluble in water but soluble in organic solvents. The water sensitive rubber compositions of the invention preferably contain on a solids weight basis from about 5% to about 50% of the solvent soluble polyurethane, and [polyurethane is used] from about 5% to 20% when a water soluble polyurethane is used.

The moisture sensitive rubber compositions of the invention are particularly useful in the manufacture of film products having controlled moisture transmission such as prophylatic devices (pessaries, condoms), surgical gloves, surgical membranes and dressings, and the like. Coatings can be prepared by spraying a substrate or article with a solvent solution or emulsion (latex) of the uncured composition which is then cured in place.

The rubber compositions of the invention can also be cast, extruded, pressed, calendered or molded

-14-

into a variety of useful shapes and configurations such as rods, bulk articles and tubing (for example, surgical catheters). Other applications are caulking and sealant materials.

5

10

15

A further use of the rubber compositions of the invention is as an active agent release medium. This is effected by adding an active agent to the uncured composition followed by curing. On exposure of such formulations to aqueous conditions, the active agents are slowly leached out in a controlled manner. Active agents which can be dispersed by this technique include biostats or biocides such as germicides, insecticides and spermicides; insect repellants; detergents including soaps; various drugs and medicines, cosmetics, fragrances, flavors and the like.

20

25

A general procedure for producing the aforescribed articles and materials comprises stripping water or solvents from the uncured polyurethane polymer/rubber blend and then pressure forming or extruding to the desired shape. Films and membranes are produced by dipping or casting, followed by curing.

The rubber compositions of the invention when cured usually exhibit an equilibrium water content of at least about 10% by weight. Equilibrium

-15-

5 water content is determined by immersing a sample of the composition in water at 20°C for 24 hours and weighing the composition in the dry state and after removal from water, and expressing the gain as % (by weight of composition) of water absorbed. The elastomer compositions thus are hydrophilic despite the inherent hydrophobicity of the rubber component.

10 The invention is illustrated further by the following examples in which components are given in parts by weight unless stated otherwise.

15 PREPARATION OF ELASTOMER/HYDROPHILIC POLYURETHANE

POLYMER COMPOSITIONS AND CURED FILMS THEREFROM

Example I

20 A rubber latex formulation was prepared as follows. To 80.0 parts of a 62.5% solids natural rubber latex were added with agitation 1.3 parts of a 68% solids sulfur dispersion, 0.3 parts of a 60% solids zinc oxide dispersion and 1.0 part of a 50%
25 solids zinc dimethyldithiocarbamate dispersion (sold as Methyl Zimate® by R.T. Vanderbilt Co.). Water, 45.0 parts was then added to reduce the latex solids level to 40%.

-16-

5 A polyurethane solution was prepared by dissolving and reacting in 588 parts of water, a hydrophilic polyurethane formed from 59.2 parts of CARBOWAX® 8000, 25.0 parts of CARBOWAX® 1450, 2.6 parts of diethylene glycol and 13.1 parts of methylene bis (4-cyclohexylisocyanate).

10 To 37.5 parts of the 40% solids rubber latex described above was added with stirring 25.7 parts of a solution of the water soluble, hydrophilic polyurethane polymer described above and 61.8 parts of water. The total solids content of the resulting mixture was 15.0% (calculated). A film was cast from this blend, air dried and cured for 20 minutes at 15 110°C.

The cured film exhibited tensile strength of 3,667 psi and an ultimate elongation of 740%. After immersion in water overnight at ambient temperature, 20 the tensile strength measured 1,799 psi with ultimate elongation of 840%.

25 0.75 inch diameter disks were die cut from the dry film and kept under water for 2 days. The disks exhibited a water content of 30% and a linear expansion of 9%. Specimens kept immersed for 12 days showed no further uptake of water.

-17-

For comparison purposes, a film was cast from the rubber latex alone, air dried and cured at 110°C for 30 minutes. This film had a tensile strength of 2,489 psi and ultimate elongation of 867%. The water content of this film after two days immersion in water was determined to be 4.5% with a linear expansion of 2.3%.

Example II

To 37.5 parts of the formulated rubber latex of Example I was added 11.4 parts of the aqueous solution of the polyurethane of Example I along with 62.1 parts of water. A film was cast, air dried and cured as in Example I. Tensile strength of the dry film was determined to be 3,966 psi with ultimate elongation of 868%. After hydrating the film for 24 hours in water at ambient temperature, the wet tensile strength was 2,658 psi and ultimate elongation 960%. Water content after two days immersion in water was found to be 21% and the linear expansion was 7%.

Water vapor transmission rates were determined on the films from Examples I and II, and compared to the values for straight natural rubbers as set forth in Table I appended. The results show the greater permeability of moisture vapors through the blend films as compared to natural rubber.

-18-

Example III

5 A styrene/butadiene latex was prepared as follows. To 72.4 parts of a 69% solids Pliolite® 5356 synthetic styrene/butadiene rubber latex (Goodyear Co.) were added 1.1 parts of a 68% solids sulfur dispersion, 0.6 part of a 60% solids zinc oxide dispersion, 0.8 part of a 50% solids Ethyl .pa Zimate® dispersion (R.T. Vanderbilt Co.) and 56. 2
10 parts water.

15 To 40.0 parts of the styrene/butadiene latex prepared above were added 11.8 parts of a 14.5% solids solution of the aqueous water soluble polyurethane of Example I along with 125.0 parts of water. A film was cast, air dried and then cured for 120 minutes at 120°C.

20 The water content of the film was determined to be 19% after two days immersion in water at ambient temperature. A film cast from the formulated and cured latex alone exhibited a water content of 9% after two days of water immersion.

25

Example IV

To 38.3 parts of the rubber latex of Example I were added 23.2 parts of an aqueous solution

-19-

containing 7.2% of a polyurethane formed from 57.6 CARBOWAX® 8000, 24.4% of CARBOWAX® 1450, 3.0 parts of diethylene glycol, 0.15% water and 14.9 parts of methylene bis(cyclohexylisocyanate).

5

A film was cast from the mixture, air dried and cured as described in Example I. The water content of the film, after two days water immersion at ambient temperature, was found to be 24% while the linear expansion was measured at 10%. Tensile strength of the wet film was 2,638 psi and ultimate elongation 840%. The water content and linear expansion values of the film remained constant after 39 days of water immersion.

15

Example V

To 25 parts of the rubber latex of Example I were added 75 parts of a 50/50 (by wt.) ethanol/water mixture and 18.7 parts of a polyurethane solution prepared by dissolving in 70 parts of a 90/10 (vol.) ethanol water mixture a polyurethane polymer formed from 54.4 parts CARBOWAX® 1450, 7.2 parts of diethylene glycol, 2.4 parts of gluconic acid delta lactone, 0.3 part water and 35.8 parts of methylenebis(cyclohexylisocyanate), followed by the addition of 70 parts of water to reduce the solids level of the solution to 17.6% and the ethanol content of the volatile portion to 45%.

20

25

-20-

5 A film was cast from the mixture, air dried and cured for 30 minutes at 110° C. After a two day water immersion at ambient temperature, the water content and linear expansion of the polymer were found to be 27% and 11%, respectively.

10 The tensile strength of the dry film was 2,054 psi and the ultimate elongation 1,100%. After two days immersion in water, the tensile strength of the wet film was determined to be 2,146 psi and the ultimate elongation 1,000%.

15 Example VI

20 To 37.5 parts of a rubber solution, formed by dissolving in 190 parts of toluene 10 parts of dry rubber produced by casting a film from the latex of Example I and drying under vacuum at 40°C, was added the following:

25 A. 12.5 parts of a 5% polyurethane solution prepared by dissolving in 95 parts of toluene, 5 parts of a polyurethane produced from 39.0 parts of CARBOWAX® 1450, 5.2 parts of ethylene glycol, 20.9 parts of polytetramethylene glycol having an average molecular weight of 2000 (available as TERATHANE® 2000 from the DuPont Co.), 0.2 part of water and 34.8 parts of methylene bis(cyclohexyl-4,4¹-isocyanate).

-21-

5 B. 1.9 parts of a dispersion of curing agents prepared by blending 2.5 parts of sulfur, 0.6 part of zinc oxide and 1 part of Methyl Zimate[®] curative in 95.1 parts of toluene on a roller mill.

10 A film was cast from the mixture, air dried and cured at 110°C for 30 minutes. After immersion for two days in water at ambient temperature, the water content of the film was found to be 18% and the linear expansion 6%.

Example VII

15 A nonaqueous blend of 70% SBR synthetic rubber and 30% water insoluble hydrophilic polyurethane was prepared by mixing the following components:

20 A. 70 parts of a synthetic rubber solution obtained by dissolving 5 parts of a cast rubber film from the Pliolite[®] 5356 SBR of Example III in 95 parts of toluene.

25 B. 3.5 parts of a curing agent obtained by forming a dispersion of 1.5 parts sulfur, 0.75 part of zinc oxide and 0.75 part of Methyl Zimate[®] dispersion in 97 parts of toluene.

-22-

C. 30 parts of the 5% polyurethane solids solution of Example VI.

5 A film was cast from the mixture, air dried and then heated to 120°C for 20 minutes. After two days immersion in water at ambient temperature, the water content of the film and its linear expansion were found to be 23% and 11%, respectively.

10 Example VIII

15 A film was cast from the blend of natural rubber latex and the aqueous solution of the water soluble polyurethane of Example I and air dried in vacuum at room temperature. The resulting uncured dried film was subjected to 5,000 psi at 50°C in a hydraulic press to form a plate 1.2 mm in thickness. After curing at 120°C for 40 minutes, the plate was
20 immersed in water for two days. The water content and linear expansion of the plate were then measured and found to be 29% and 9%, respectively.

25 A key property of elastomers for many applications is good tear resistance. Table II appended summarizes the wet tear propagation resistance values found for some of the rubber/hydrophilic compositions of the invention. These values were determined following ASTM 1938. As

-23-

will be observed from the Table II data, the rubber/hydrophilic polyurethane compositions of the invention exhibited wet tear propagation resistance approximating that of cured natural rubber. Yet, at the same time the hydrophilic character of such composition was retained, greatly exceeding that of rubber alone as demonstrated by the high water absorption capacity of the compositions. Hydrophilic properties mean good water vapor transmission rate, a highly desirable quality of such film products as condoms and surgical gloves.

OTHER USES OF THE ELASTOMER/HYDROPHILIC

COMPOSITIONS

EXAMPLE A = Extruded Tube

A blend of the rubber latex and water insoluble hydrophilic polyurethane of Example V was cast as a film and air dried under vacuum at 30°C to constant weight. The resulting dry uncured film was cut into small (5x5 mm) pieces and the pieces fed into a laboratory hand extruder preheated to 60°C. A tube having an OD of 7 mm and an ID of 4 mm was extruded at 12,000 psi. The tube was suspended in an oven and cured at 120°C for 60 minutes. After immersion in water for two days at ambient temperature, the water content and linear expansion were determined and found

-24-

to be 26% and 10%, respectively. The tube is suitable for use as a urinary catheter or drain tube for body fluids.

5 EXAMPLE B = CONDOM

 To the rubber latex and hydrophilic polymer blend described in Example V was added 0.2 parts of nonylphenoxypoly (ethyleneoxy) ethanol nonionic
10 surfactant (IGEPAL® CO 630, GAF Corp.). Glass mandrels used for forming latex condoms were used to dip condoms from the above solution. After each dip, the latex solution was air-dried at room temperature. After the fourth dip, the condoms were cured at 100°C
15 for 20 minutes. When put into water, 20 mg of the IGEPAL® CO 630 surfactant was released during the first hour.

20 EXAMPLE C = Active Agent Release Medium

 To the mixture of rubber latex and hydrophilic polymer of Example A was added 0.5 parts of tetracycline. The mixture was processed, dried and extruded as described in Example A. The resulting
25 tube was placed in distilled water at 37°C and the elution of tetracycline was monitored every hour by taking samples from the mixed solution. It was found that the tetracycline elution was fairly steady at 4-6 mg/hour during the 24 hour period.

-25-

TABLE I

5	Film		Hydrophilic	Moisture Vapor
	Thickness	Polyurethane	Transmission Rate	
	<u>Film</u>	<u>(inch)</u>	<u>%</u>	<u>(g/m²/24 hours)</u>
10	Example I	0.0129	20	454
	Example II	0.0231	10	120
	Rubber	0.0174	0	69
15	Rubber	0,0260	0	53

20

25

-26-

TABLE II

	Film Tested	% Hydro- philic Polyurethane	Thickness (inch)	Tear Propaga- tion Average (lb/in)	Resis- tance Maximum
5					
	Example II	10	0.0134	35.1	97.3
10	Example IV	10	0.0165	34.9	92.3
	Example V	25	0.0152	35.9	98.5
15	Cured rubber	0	0.0229	35.3	110.8

20

25

-27-

Claims:

1. A moisture sensitive elastomer composition comprising a homogenous blend of a curable rubber component and a hydrophilic polyurethane, said composition upon curing having an equilibrium water absorption of at least 10% by weight.
2. The composition of claim 1 wherein the rubber component is a natural or synthetic rubber.
3. The composition of claim 1 wherein the hydrophilic polyurethane is formed by reacting a diisocyanate with a mixture of a low molecular weight alkylene glycol and one or more water-soluble polyoxyalkylene (C²-C⁴) glycols having a number average molecular weight of from about 400 to about 20,000, and wherein the equivalent ratio of isocyanate to hydroxyl groups is from about 0.5:1 to about 1:1 and the percent by weight of isocyanate is from about 5% to about 60%.
4. The composition of claim 1 wherein the polyurethane is insoluble in water but soluble in organic solvents, and is present in the composition in an amount of from about 5% to 50% by weight.
5. The composition of claim 1 wherein the polyurethane is soluble in water and organic solvents,

-28-

and is present in the composition in an amount of from about 5% to about 30% by weight, the said composition having an equilibrium water content of at least 15% by weight.

5

10

6. The composition of claim 2 wherein the synthetic rubber is selected from the group consisting of polyisoprene, polybutadiene, polychloroprene, butadiene/styrene copolymer, isobutene/isoprene copolymer and ethylene/polypropylene/butadiene terpolymer.

15

7. A cured composition as in claim 1 in the form of a prophylactic.

8. A cured composition as in claim 1 in the form of a pessary.

20

9. A cured composition as in claim 1 in the form of a film.

10. A cured composition as in claim 1 in the form of a sealant.

25

11. The composition of claim 9 wherein the film is in the form of a bandage.

12. The composition of claim 9 wherein the film is in the form of a glove.

-29-

13. A cured composition as in claim 1 in the form of an extruded shape.

5 14. The composition of claim 13 wherein the extruded shape is in the form of a tube.

10 15. An active agent release medium comprising an active agent and a moisture sensitive elastomer composition as in claim 1.

16. The active agent release medium of claim 15 wherein the active agent is a drug.

15 17. The active agent release medium of claim 15 wherein the active agent is a fragrance.

20 18. The active agent release medium of claim 15 wherein the active agent is a cosmetic.

19. The active agent release medium of claim 15 wherein the active agent is a biocide.

25 20. The active agent release medium of claim 19 wherein the biocide is a germicide, an insecticide or a spermicide.

-30-

21. The active agent release medium of claim 15 wherein the active agent is an insect repellent.

5 22. The active agent release medium of claim 15 wherein the active agent is a detergent.

10 23. A process of producing a moisture sensitive elastomer composition having, upon curing, an equilibrium water absorption of at least 10% by weight comprising forming a curable homogeneous blend of a rubber latex and a hydrophilic polyurethane and subjecting the blend to curing conditions.

15 24. The process of claim 23 wherein the rubber latex is natural rubber latex.

 25. The process of claim 23 wherein the rubber latex is a synthetic rubber latex.

20 26. The process of claim 23 wherein prior to curing the blend is subjected to shaping.

25 27. The process of claim 26 wherein the blend is shaped by injection molding, extrusion, pressing or calendering.

 28. The elastomer composition prepared by the process of claim 23.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/03577

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC (4): CO8L 75/08; A41D 19/00 US. CL. 525/131, 937; 2/168																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border: 1px solid black; text-align: left;">Classification System</th> <th style="border: 1px solid black; text-align: left;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">US.</td> <td style="border: 1px solid black; vertical-align: top;">525/131, 937 2/168</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	US.	525/131, 937 2/168											
Classification System	Classification Symbols																
US.	525/131, 937 2/168																
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border: 1px solid black; text-align: left;">Category [*]</th> <th style="width: 70%; border: 1px solid black; text-align: left;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border: 1px solid black; text-align: left;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">X</td> <td style="border: 1px solid black; vertical-align: top;">JP, A, 62-57457 DAINICHISEIKA 13 MARCH 1987 (SEE ABSTRACT)</td> <td style="border: 1px solid black; vertical-align: top;">1-14</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">WO, A, WO8605796 HAEFFNER 9 OCTOBER 1986 (SEE PAGE 1, LINES 25-28 AND CLAIMS)</td> <td style="border: 1px solid black; vertical-align: top;">1-14, 23-28</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">GB, A, 2,150,938 GOULD 10 JULY 1985 (SEE PAGE 2, lines 57-63)</td> <td style="border: 1px solid black; vertical-align: top;">15-22</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top;">A</td> <td style="border: 1px solid black; vertical-align: top;">US, A, 4,563,490 STOL 7 JANUARY 1986 (SEE COL. 2, LINES 54-57 AND COL. 5, LINES 43-65)</td> <td style="border: 1px solid black; vertical-align: top;">15-22</td> </tr> </table>			Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	JP, A, 62-57457 DAINICHISEIKA 13 MARCH 1987 (SEE ABSTRACT)	1-14	A	WO, A, WO8605796 HAEFFNER 9 OCTOBER 1986 (SEE PAGE 1, LINES 25-28 AND CLAIMS)	1-14, 23-28	A	GB, A, 2,150,938 GOULD 10 JULY 1985 (SEE PAGE 2, lines 57-63)	15-22	A	US, A, 4,563,490 STOL 7 JANUARY 1986 (SEE COL. 2, LINES 54-57 AND COL. 5, LINES 43-65)	15-22
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³															
X	JP, A, 62-57457 DAINICHISEIKA 13 MARCH 1987 (SEE ABSTRACT)	1-14															
A	WO, A, WO8605796 HAEFFNER 9 OCTOBER 1986 (SEE PAGE 1, LINES 25-28 AND CLAIMS)	1-14, 23-28															
A	GB, A, 2,150,938 GOULD 10 JULY 1985 (SEE PAGE 2, lines 57-63)	15-22															
A	US, A, 4,563,490 STOL 7 JANUARY 1986 (SEE COL. 2, LINES 54-57 AND COL. 5, LINES 43-65)	15-22															
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">27 JANUARY 1989</div> </td> <td style="width: 50%; border: 1px solid black; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">15 MAR 1989</div> </td> </tr> <tr> <td style="border: 1px solid black; vertical-align: top;"> International Searching Authority <div style="text-align: center;">ISA/US</div> </td> <td style="border: 1px solid black; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;"> A. CARRILLO </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">27 JANUARY 1989</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">15 MAR 1989</div>	International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;"> A. CARRILLO </div>											
Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">27 JANUARY 1989</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">15 MAR 1989</div>																
International Searching Authority <div style="text-align: center;">ISA/US</div>	Signature of Authorized Officer <div style="text-align: center;"> A. CARRILLO </div>																

THIS PAGE BLANK (USPTO)